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Chemical Considerations Underlying the Manufacture of Portland Cement.

By W. WATSON, B.Sc., and Q. L. CRADDOCK, M.Sc.

THE properties of the various compounds which may be present in Portland cement clinker have been dealt with earlier in this series of articles. In this article consideration is given to the directions from which high-strength cements may most likely be obtained by modification of the composition of the raw mixtures. Since the four major constituents of cement are lime, silica, alumina, and iron oxide, the composition of the raw material mixture may be fixed by the ratios

$$\begin{aligned}
 (1) \dots & \frac{\text{mols CaO}}{\text{mols SiO}_2 + \text{mols Al}_2\text{O}_3 + \text{mols Fe}_2\text{O}_3} \quad (2) \dots \frac{\% \text{SiO}_2}{\% \text{Al}_2\text{O}_3 + \% \text{Fe}_2\text{O}_3} \\
 (3) \dots & \frac{\% \text{Al}_2\text{O}_3}{\% \text{Fe}_2\text{O}_3}
 \end{aligned}$$

By consideration of each of these ratios it should be possible to arrive at the ideal composition from the practical point of view. The influence of MgO will be considered later apart from these ratios.

(A).—Influence of the Lime Ratio.

The molecular ratio $\frac{\text{CaO}}{\text{SiO}_2 + \text{R}_2\text{O}_3}$ gives the actual basicity of the raw mixture and will be called "the theoretical lime ratio." The lime ratio specified in the British Standard Specification for Portland Cement is the molecular ratio

$\frac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$, while the hydraulic modulus, frequently referred to in United States publications, is a percentage ratio $\frac{\% \text{CaO}}{\% \text{SiO}_2 + \% \text{Al}_2\text{O}_3 + \% \text{Fe}_2\text{O}_3}$. All three are in common use, and this has sometimes led to misunderstanding where it is not stated which particular "lime ratio" is referred to. Throughout this article reference to the lime ratio means the theoretical lime ratio.

It is generally agreed that the lime ratio should be maintained as high as possible consistent with soundness. Not only does this increase the strength at short dates, but it also renders the clinker easier to grind. Experience shows, however, that although both tensile and crushing strengths increase gradually with the lime ratio, at a certain point, dependent upon the nature of the raw material and upon its composition, the tensile strength decreases although the crushing strength continues to increase. When the limits of soundness are being approached, however, the crushing strength also falls. Where this limit will occur can only be arrived at by practical experience, since it largely depends upon the proportions of silica, alumina, and iron oxide in addition to the type of kiln and other burning conditions. It has also been shown that in order that the lime content can be raised without danger of unsoundness in the resulting cement, the raw mixture should be finely ground. This applies particularly to a chalk and clay mixture since the silica present in the former occurs in the form of flints which, unless finely ground, are difficult to combine with the lime. Having increased the lime ratio and ground the raw materials more finely it only remains to have careful control over the clinkering process and to grind the resulting clinker more finely to obtain the best results possible with a simple two-component mixture. Kühl¹⁸ has pointed out that cases of decreased strength on finer grinding of the raw material have been observed, due to the fact that the lime ratio has not been increased. Although a more homogeneous mixture is obtained by finer grinding, unless the lime content is raised the coarse raw mixture will give a clinker containing portions richer in lime than the finely-ground mixture if the lime content of the latter is not raised. In such cases the influence of the portions of clinker rich in lime is sufficient to give a cement which will develop a higher strength than one low in lime throughout. Experience shows that most mixtures can be used with a theoretical lime ratio of about 2.70 to 2.75 provided they are sufficiently finely ground, although the actual limit will depend upon the nature and composition of the raw materials.

(B).—Influence of Silica Ratio.

It is generally agreed^{20, 21} that when this ratio, $\frac{\% \text{SiO}_2}{\% \text{Al}_2\text{O}_3 + \% \text{Fe}_2\text{O}_3}$ rises to a high figure (3 or more) the cement becomes slow setting. Cements with a silica ratio of 2.7 or more are usually slow hardening, but show a progressive gain. On the other hand, a cement with a silica ratio of 1.8 or less is usually rapid hardening. Candlot¹ points out that high-early-strength cements, resistant to sea water, can be obtained by lowering the silica ratio by the addition of alumina or equal parts of alumina and iron oxide. Nagai and Akoyama² made cements of low silica ratio and found the highest early strengths were obtained with the highest alumina and iron oxide contents (3.5 to 4.5 per cent. of both alumina and iron oxide).

Other things being equal, the following may be said of the influence of silica in the manufacture and in the quality of Portland cement: (1) Highly siliceous raw materials are hard to burn; (2) Highly siliceous raw mixtures, unless finely

ground, combine with difficulty; (3) Siliceous raw mixtures containing silica in soluble form combine more readily in the kiln than do raw mixtures containing all or part of the silica in the insoluble form, such as flints. Also too much free crystalline silica lowers the plasticity of the mixture, making the latter sandy or dusty, and hinders uniform clinkering; (4) Siliceous clinker is uniformly small in size; (5) Cements with very high silica ratios are of a slow setting nature. They are slow hardening, but show progressive gain; (6) The more siliceous the cement, the more resistant it becomes to injurious external influences.

(C).—Influence of Alumina/Iron Oxide Ratio.

Diverse opinions exist as to the influence of varying this ratio upon the quality of the cement. General experience seems to be that although high-alumina-content cements give the best strength results in the laboratory the high iron oxide cements result in the best concrete in practice. It is usually found, however, that, other things being equal, the effect of increasing the iron oxide content at the expense of alumina is to lengthen the time of set.²¹ The effect upon the strength is not, however, agreed upon to the same extent.

Schott²² prepared a cement containing only lime, silica, and iron oxide and obtained a slow setting but sound product. Newberry¹⁹ confirmed this by preparing a mixture of the composition $3\text{CaO} \cdot \text{SiO}_2 + 2\text{CaO} \cdot \text{Fe}_2\text{O}_3 (\text{Fe}_2\text{O}_3 = 7\%)$ which when clinkered and ground gave a slow-setting sound product which was quite hard when set. Leduc,³ however, claimed that cements in which all the alumina is replaced by iron oxide are mechanically weak.

At the other extreme, where all the iron oxide is replaced by alumina, Clifford Richardson⁴ has shown that good Portland cement can be made by using only lime, silica, and alumina in the correct proportions.

Campbell⁵ showed that the ferrites are hydraulic and that part of the alumina in calcium aluminates can be replaced by ferric oxide yielding mixed crystals which show very good strength. He found that cement containing no alumina was very slow setting while a similar cement containing no iron oxide was rapid hardening.

Kühl⁶ concluded from his experiments that: (1) Ferric oxide acts as a flux in the burning of Portland cement clinker. It both lowers the burning temperature and increases the sintering range, thus making commercial operation easier. Formation of readily-fusible iron compounds probably takes place, and these act as a solvent in which the reaction of clinker formation takes place. (2) Alumina is not an essential component of an hydraulic cement. (3) Practically all cements with increased iron content are slow-setting. (4) A test mixture entirely free from alumina burned to a good clinker, although the resulting cement was slightly below the average for good quality cements as regards strength.

In connection with (1), Nagai and Asaoka⁷ point out that iron cements containing only very small amounts of alumina and large amounts of iron sinter at 1,450 to 1,500 deg. C., which is about the corresponding temperature for normal Portland cement clinkers. This, they state, is due to the small amount of calcium aluminate and to the lack of eutectic formation. Nagai⁸ found that partial

replacement of alumina by iron oxide reduces the absolute strength but in addition diminishes the deterioration on water curing and prevents the dusting of the clinker. Kühl¹⁸ has pointed out that higher strengths are obtained from cements with high silica ratios (3 to 4) and from those with low silica ratios (1.2 to 1.4), whilst cements representing the middle range of this ratio (1.4 to 3) give somewhat lower strengths with the same lime ratio. He does not appear to attach much importance to the alumina iron-oxide ratio, so far as strength is concerned, but finds that with a high value for this ratio (the silica ratio being low) the cements tend to be unreliable as regards setting time, tending to become quick setting. He overcomes this difficulty by increasing the iron oxide content, thereby reducing both the silica and alumina/iron-oxide ratios. Normally cements with a high silica ratio tend to be slow hardening, and in order to counteract this the alumina/iron-oxide ratio should be high, thereby giving a larger proportion of rapid-hardening aluminates. On the other hand, with low silica-ratio cements which are relatively quick setting the proportion of alumina to iron oxide may be low. The only difficulty is the fact that the clinker readily becomes plastic, tending to the formation of clinker rings. Careful control of the burning conditions will overcome this, however, and a corresponding saving in fuel consumption is usually experienced.

To summarise, it may be said that the value of the silica ratio and alumina/iron-oxide ratio must be considered together, increase in one ratio necessitating a corresponding increase in the other.

Variations of the alumina/iron oxide ratio only appear to have been practised in one direction on a commercial scale, namely in the reduction of the ratio. Possibly this can be explained by the difficulty in obtaining a cheap source of alumina, whereas ample supplies of iron ores are available. Additions of iron oxide to the raw materials have been known to give good results in Germany,²¹ Mexico⁹ and the Balkans.¹⁰ As already stated, although these high-iron-cements are slow setting they harden fairly rapidly, giving high initial strengths. They differ from ordinary high-strength cements in that the compression and tensile strength bear practically a constant ratio to each other, the compression strength being approximately ten to twelve times the tensile strength.

In Mexico, Blank⁹ has shown that by reducing the alumina/iron-oxide ratio it is possible to increase normal kiln output by 12 per cent. and upwards, depending on the extent of the reduction of the ratio. With high-iron cements it is possible to increase the quality of the cement from an ordinary Portland to a high-early-strength cement without further grinding of the raw materials, without harder burning of the clinker, and without further grinding of the clinker over that which has been hitherto customary using normal mixes. He also states that this high-iron clinker is easier to grind than normal clinker of the same lime ratio.

Kühl¹⁰ mentions a case in the Balkans of improvement of cement quality by addition of iron oxide. The ordinary clinker always dusted and the cement was of poor quality. The clay employed only contained 4 per cent. Al_2O_3 . Addition of an iron mineral containing 68 per cent. Fe_2O_3 and 22 per cent. SiO_2 was made

in the proportions of 100 parts marl, 30 parts clay, and 3 to 4 parts iron ore. The resulting clinker was stable and the cement very satisfactory; it contained 4.67 per cent. Al_2O_3 and 4.73 per cent. Fe_2O_3 .

Nagai and Akoyama¹¹ experienced similar improvements on the additions of pozzolana rich in iron to the raw materials, and high-strength cement was obtained.

An "Erz Cement" is manufactured in Germany from siliceous limestone and iron ore.²¹ This cement is distinguished by its high initial strength and in its exceptional resistance to the action of sea water.

As early as 1909 Spencer and Eckel²³ patented a process for the preparation of iron cements in America. They describe a cement in which iron oxide is substituted wholly or in part for the alumina ordinarily present, and claim that concrete made from this cement is very resistant to sea water. Whilst in the ordinary way such cements have obtained their iron from the rich iron-oxide ores used in other industries, the patentees propose the use of a cheap, natural, and easily-fused silicate of iron and potassium called "Glaucinite" or the related mineral "Greenalite," both of which have the common name of "Greensand." The patent specifically includes any mineral containing sufficient amounts of iron silicate for the purpose of the invention.

(D).—Influence of Magnesia.

The presence of abnormal quantities of magnesia in certain brands of Portland cement has led workers to investigate the influence of this component upon the quality of the cement. The Newberrys,¹⁹ in the course of their investigations on the synthetic mixtures, showed that mixtures of alumina and silica with various amounts of magnesia when burned gave, in all cases, non-hydraulic products. A mixture of dolomitic limestone, silica, and alumina was made in which enough lime was present to combine with the acidic materials, leaving the magnesia unaccounted for. The product, after burning and grinding, set and hardened normally and was sound, although the molecular ratio $\text{CaO} + \text{MgO}/\text{SiO}_2 + \text{Al}_2\text{O}_3$ was 4.16. Thus MgO cannot be assumed to act equally and equivalently with CaO. Moreover, they showed that magnesia combines with the silica and alumina of the clay to a very much less extent than does lime.

According to Klein and Phillips²⁴ magnesia can exist in Portland cement in amounts as great as 7.5 per cent. before any new compound not present in normal clinker appears, i.e. it forms homogeneous compounds or solid solutions with either $\beta - 2\text{CaO} \cdot \text{SiO}_2$ or $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ below this percentage. They could detect no free magnesia in their preparations even with high MgO contents. Hansen¹², however, in his researches on the system $2\text{CaO} \cdot \text{SiO}_2 - \text{MgO} - 5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ concluded that MgO forms solid solutions neither with $2\text{CaO} \cdot \text{SiO}_2$ nor with $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and that it cannot replace CaO in these compounds. Zulkowski¹³ could not obtain a cement of the composition $2(2\text{MgO} \cdot \text{SiO}_2) + 2\text{MgO} \cdot \text{Al}_2\text{O}_3$ by burning the correctly proportioned mixture, although similar burns with CaO in place of MgO gave good cements. Thus MgO is not molecularly equivalent to CaO in Portland cement. He found free MgO in the product and

concluded that only a very high temperature would have produced complete combination.

Bates²⁵ found that when the percentage of MgO reached 8 per cent. monticellite ($\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$) was noted in cements of otherwise normal composition. With a further increase of 2 per cent. spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$) appeared, and finally, when the percentage of magnesia reached 20 to 25 per cent., some free MgO was noted. The results of burns of various compositions show that the amount of $\beta\text{-2CaO} \cdot \text{SiO}_2$ decreases with increased amounts of MgO. Apparently the monticellite, which increases with increased amounts of MgO, was formed at the expense of the orthosilicate, although the amount of $3\text{CaO} \cdot \text{SiO}_2$ was not materially reduced. The formation of monticellite and spinel would account for the large amount of insoluble residue present in high-magnesia cements, since both are largely insoluble in dilute acid.

Glaserapp¹⁴ considers that magnesia remains free in cements burned at ordinary temperatures by reason of its high melting point. There does not appear to be any evidence definitely contradicting this statement up to a content of 8 per cent. MgO. It has been noted¹⁶, however, that Portland cements containing only 6 per cent. MgO may show appreciable expansion at the end of several years, although they are sound when subjected to an accelerated test and have a normal expansion in water during the first year. This seems to indicate some instability due to magnesia. Campbell¹⁵ studied the rate of hydration of MgO obtained by burning magnesite at various temperatures. He found that the decomposition of magnesium carbonate is complete at 600 deg. C. and the hydration of the MgO burned at this temperature is complete in three days. The results of his other experiments may be summarised as follows: (1) All samples burned at or below 1,100 deg. C. hydrate completely within three months. (2) Between 1,100 and 1,200 deg. C. a change sets in which results in a slower rate of hydration. Samples burned at 1,200 deg. C. hydrate very slowly, complete hydration being attained after three years. (3) Samples burned at above 1,200 deg. C. hydrate very slowly and are not completely hydrated after six years. (4) The burning temperature and percentage hydration at the end of six years are as follows: 1,300 deg. C., 83.5 per cent.; 1,400 deg. C., 81.0 per cent.; 1,450 deg. C., 70.3 per cent. Earlier results indicated that burning at 1,450 deg. C. results in 61 per cent. hydration after 18 months.

These results offer a ready explanation for the expansion of high-magnesia cements after being immersed in water for several years. It is this slow development of expansion which renders the use of cement containing abnormally high percentages of magnesia so dangerous, for up to 6 per cent. MgO neither the early strength nor the setting properties are affected. Tests made by Bates²⁵ on neat and mortar specimens stored in water after 24 hours in the damp chamber showed that the MgO content can be increased to 7 per cent. before there is any noticeable falling off in strength, and with cements containing lower amounts of alumina and silica the magnesia content can be a little higher than 7 per cent. Cements with more than 10 per cent. MgO give low early strength, although only

those cements with more than 18 per cent. MgO showed pronounced disintegration at the end of one year. At the end of three years all the cements with more than 10 per cent. MgO were enlarged and cracked. Examination of those disintegrated specimens showed that the cracks and cavities were filled with crystals of hydrated lime, magnesium hydrate, and sometimes calcium sulphoaluminate. The delayed expansion appears to be due to the slow liberation of free magnesia as shown by Campbell's experiments. According to Bates,²⁵ if the magnesia content is greater than 8 per cent. in the cement, monticellite and spinel are formed, and he accounts for the presence of $Mg(OH)_2$ in the disintegrated specimens as being due to the hydration of these compounds.

Dyckerhoff¹⁶ found that the expansion of cements is approximately proportional to the percentage of magnesia in the cement. He considers that up to 6 per cent. MgO may be safely present in cement. Above this point a high expansion coefficient results, with a corresponding lower tensile strength.

Bates²⁵ also found that high magnesia cements develop a quick set accompanied by the evolution of a large amount of heat. This he ascribes to the increase in the proportion of quickly-hydrating compounds at the expense of slowly-hydrating material, i.e. $3CaO.SiO_2$ and $3CaO.Al_2O_3$ increased at the expense of $2CaO.SiO_2$ and lower aluminates. This assumes that a large amount of the silica and alumina combines with the magnesia to form monticellite and spinel. He also found that concrete made with cement containing large amounts of magnesia did not disintegrate in certain salt solutions to such an extent as did those made from cements of moderate magnesia content.

It has been suggested that magnesia added to the raw materials produces a fluxing action on burning and thus reduces the clinkering temperature. Blank¹⁷ produced Portland cement raw mixtures containing 8 to 19 per cent. MgO, but found that they balled together on burning in the rotary kiln. Although the cement had good strength it ultimately crumbled. He found that the best cements of the high-magnesia class were to be obtained in the region of 6.2 to 7.6 per cent. MgO.

Bates found that with marked increase in MgO content the difficulties of burning the raw materials increased considerably. This was very marked when the percentage of magnesia increased beyond 9.5 per cent. The clinker dusted badly even when it was decidedly overburnt, and the formation of rings in the kiln was also excessive. Increased percentages of magnesia did not appear to decrease the clinkering temperature, yet the "softening" point was decidedly lowered. Above 9.5 per cent. MgO the clinker was of a reddish-yellow appearance which, when ground, gave a yellow-tinted cement and a muddy plastic concrete.

In recent years it has been claimed that high-magnesia cements favour rapid hardening. Several patented processes are being worked on this basis, the main feature of all of them being that the calcining and clinkering processes are intensified, even to the point of double burning according to some patents. Balthasar, in British patent 309069/29, claims to produce a Portland cement of high initial strength from materials containing magnesia, such as blast furnace

slag, by intensifying the calcination to above 1,450 deg. C. for at least 20 minutes to produce a clinker containing 5 to 15 per cent. MgO. The idea underlying the process seems quite feasible, since the magnesia introduced will combine with some of the silica and alumina if heated at a high enough temperature and for a sufficient time, thereby producing higher-limed compounds. The danger, however, of producing quick-setting properties and unsound cements needs to be guarded against.

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Improvements in Firing with Pulverised Coal. By H. Jordan. (*Zement*, 1935, pp. 127, 147).—This paper deals with German patents on firing with pulverised coal taken out between July, 1933 and July, 1934.

Determination of Cement in Mortar. By A. Steopoe. (*Zement*, 1935, p. 758).—The amount of cement in a mortar is found by determining the soluble silica by treatment of the pulverised mortar with normal hydrochloric acid and the residue from this with 5 per cent. sodium carbonate, both in the cold. Both these reagents should be mixed with 5 per cent. sodium chloride to keep the filtrate clear. Washing is done with 0.8 per cent HCl. The silica is determined in the filtrate in the usual way. The amounts of silica soluble in acid and in alkali should be determined separately, because if the latter is greater than 1 per cent. it shows that soluble silica other than from the cement is present and in this case the method is not applicable. If the soluble silica in the cement is known the cement content of the mortar can be calculated.

Studies on Ore, or Iron, Cement.

By SHOICHIRO NAGAI and KEIMA MATSUOKA.

IN continuation of their studies on the preparation and the hydraulic properties of so-called ore cement (Erzzement) or iron cement (Eisenzement), a type of high-iron-oxide special Portland cement, the authors give the following information in a paper presented to the Institute of Silicate Industry, Tokyo Imperial University.

One of the high-iron-oxide special Portland cements known as "Kalicrete," proposed by Thorvaldson and Flemming, contains alumina and iron oxide in nearly equal quantities of 4 to 4.5 per cent., i.e., about 13 per cent. of celite ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$) and about 3.5 per cent. of tricalcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$). The alumina content is thus a little larger than the equimolecular proportion to iron oxide for the formation of celite. The present authors, by increasing the content of iron oxide, made two raw mixtures of modified type of "Kalicrete" cement from raw materials of limestone, clay, ganister, and copper slag, as shown in Table 1.

TABLE 1

				(VI a) Raw Mixture.	(VI b) Raw mixture.
				Per cent.	Per cent.
Loss on ignition	33.19	32.61
SiO ₂	14.91	15.58
Al ₂ O ₃	2.74	2.84
Fe ₂ O ₃	4.16	4.35
CaO	43.74	43.21
MgO	1.02	1.06
Total	99.76	99.65

By using these two mixtures several series of comparative tests were carried out to study the degree of combination between lime and silica, alumina, iron oxide, etc., by determining the amounts of residual free lime and insoluble residue of acid components. The heating temperatures were 1,300 to 1,350 deg. C., and the heating time one hour. The results are shown in Table 2.

TABLE 2

No. of experiment.				Raw mixture.	Heating temperature.	Heated product.	
						Free lime.	Insoluble residue.
(41)	VI a	(deg. C.) 1,300	Per cent. 4.02	Per cent. 0.16
(42)	VI a	1,350	—	0.08
(43)	VI b	1,300	2.16	0.12
(44)	VI b	1,350	—	0.06

As seen from these results, for the formation of "Kalicrete" cement, heating at 1,350 deg. C. was sufficient.

By using the preliminary studies these high-iron-oxide special Portland cements, i.e., two iron cements and one "Kalicrete" cement, were prepared from raw materials of limestone, clay, ganister and copper slag. The raw mixtures were moulded with water into spheres of 15 mm. diameter, dried in air, and burned to clinker at 1,350 to 1,360 deg. C. in a gas furnace. The three clinkers were ground to cement with 2.5 per cent. gypsum, and had the physical properties, chemical compositions, and hydraulic compounds, calculated by the formula (a) proposed by the authors, and formula (b) proposed by R. H. Bogue, as shown in Table 3.

TABLE 3.

				Iron cement. (II Bb).	Iron cement. (V)	" Kalicrete " cement. (VI a).	
Fineness	4.900	..	per cent.	1.4	1.2	1.1	
	Loss on ignition..	..	"	0.18	0.19	0.20	
	Insoluble residue	..	"	0.03	0.03	0.02	
	SiO ₂	..	"	21.92	21.90	21.62	
	Al ₂ O ₃	..	"	2.72	2.66	3.95	
	Fe ₂ O ₃	..	"	7.42	7.37	6.10	
	CaO	..	"	65.08	60.86	64.80	
	MgO	..	"	1.08	5.31	1.46	
	SO ₃	..	"	1.26	1.28	1.24	
	Total	..	"	99.69	99.59	99.41	
Hydraulic compounds				(a)	(b)	(a)	(b)
	2CaO.Fe ₂ O ₃	..	"	12.6	5.4	12.6	5.5
	4CaO.Al ₂ O ₃ .Fe ₂ O ₃	..	"	—	13.0	—	12.7
	3CaO.Al ₂ O ₃	..	"	7.2	—	7.0	—
	2CaO.SiO ₂	..	"	21.5	16.7	33.7	29.2
	3CaO.SiO ₂	..	"	54.9	61.3	38.7	44.6

As seen from these results, iron cement (V) contains a little more 2CaO.SiO₂ and less 3CaO.SiO₂, owing to the presence of 5.3 per cent. magnesia and 60.9 per cent. CaO.

The three samples were tested for their hydraulic properties by comparing their tensile and compressive strengths and expansion or contraction. The results were compared with those of three commercial cements, i.e., one ordinary Portland cement, one blastfurnace slag cement and one mixed Portland cement of "Neo-solidit" type. The results of the strength tests are shown in Table 4, and those of expansion or contraction in Table 5.

TABLE 4.

No. of cement	Type of cement	Water-cement ratio	Bending Strength, (kg. per sq. cm.)					Compressive strength, (kg. per sq. cm.)					Valuation Number (Cw + 10B)
			3 days	7 days	28 days	Comb. 28 days	Total (B × 10)	3 days	7 days	28 days	Comb. 28 days	Total	
(II Bb)	Iron cement	57	36.9	56.2	81.6	83.8	2,585	118	236	542	397	1,203	3,878
(V)	Iron cement	57	31.8	44.3	74.6	74.6	2,253	85	160	293	309	847	3,100
(VI a)	"Kalicrete"	57	41.3	60.6	83.6	85.8	2,713	148	272	466	474	1,360	4,073
No. 246	Portland cement	60	36.2	48.1	69.2	75.2	2,287	120	193	353	364	1,030	3,317
No. 238	Blastfurnace slag cement	58	52.4	71.3	83.2	99.8	3,067	207	365	530	528	1,630	4,697
No. 242	"Neo-solidit"	63	37.9	43.0	73.4	68.9	2,232	133	189	368	349	1,039	3,271

It is seen that iron cements are slow-hardening cements, while "Kalicrete" cement hardens a little earlier. No. 246 ordinary Portland cement was extremely slow-hardening, which is rare in Japanese cements, owing to its chemical compositions and hydraulic compounds (SiO_2 ; 22.08 per cent.; Al_2O_3 , 6.13 per cent.; Fe_2O_3 , 2.76 per cent.; total CaO , 63.40 per cent.; MgO , 2.38 per cent.; free CaO , 2.72 per cent.; combined CaO , 60.7 per cent.; $3\text{CaO} \cdot \text{SiO}_2$, only 22.8 per cent.; $2\text{CaO} \cdot \text{SiO}_2$, 46.1 per cent. of low-heat or low-temperature cement type).

TABLE 5.

No. of cement.	Type of cement.	Water-cement ratio per cent.	Expansion (+) or contraction (-), (mm/10 m).					Boiled 3 hours after 28 days.
			3 days.	7 days.	28 days.	Comb. 28 days.		
(II Bb)	Iron cement	57	+1	+1	+1	-3	0	
(V)	Iron cement	57	+1	+2	+2	-3	+1	
(VI a)	" Kalicrete "	57	+1	+1	+1	-3	0	
No. 246	Portland cement ..	60	+2	+3	+3	-3	+2	
No. 238	Blastfurnace slag cement	58	+1	+2	+2	-4	+2	
No. 242	" Neo-soliditit " ..	63	+1	+2	+2	-4	+1	

It is seen that iron cement and "Kalicrete" cement are as stable as other types. No. 246 Portland cement is a little unstable owing to the large amount of uncombined or free lime (2.72 per cent.), No. 242 "Neo-solidit" cement is a little expansive, owing to the large amount of admixture of siliceous nature (30 to 40 per cent.), and (V) iron cement expanded a little owing to the large amount of uncombined or free magnesia (5.3 per cent.).

These six cement samples of various types were tested for temperature rise on setting and hardening by the method of measuring temperature rise of cement paste in a small Dewar glass vessel. Iron cements (IIBb) and (V) are seen to generate the least heat, and are suitable for mass concrete.

The authors are continuing the comparison of these high-iron-oxide special Portland cements with several mixed Portland cements, by studying their resistance to various salt solutions of NaCl , MgCl_2 , Na_2SO_4 , MgSO_4 , etc.

Trass and Free Calcium Hydroxide. By W. Wittekindt. (*Tonindustrie Zeitung*, 1935, p. 139).—The amounts of calcium hydroxide liberated during the setting of Portland cement have been compared with those from trass, blast-furnace, and iron Portland cements. Though at early dates trass does not combine with the lime liberated, it does so to considerable extent later on. Mixtures of calcium hydroxide and trass, ground brick, and slag were tested and it was found that the trasses (Brohl valley and Nette valley) were the best and afforded the greatest resistance to corrosion.

The Future of Cement Research.

IN a recent number of *Industrial and Engineering Chemistry*, Mr. R. W. Carlson, of the Massachusetts Institute of Technology, states:

Looking into the future, as far as the properties of cement are concerned, one sees research activities shifted from attempts to produce a cement that will make concrete stronger and stronger, to one that will make concrete more and more durable and more and more constant in volume. Then, and only then, will concrete be the efficient building material that its strength and casting qualities entitle it to be.

In trying to produce cement that will make concrete more durable and constant in volume, the research worker will continue to learn more about the fundamentals of cement. He will learn the physical and chemical make-up of representative cement grains. He will not be content with microscopic examinations, but he will determine also the atomic structure by means of X-rays. He will learn what changes take place in the hydration process, not only in shape and appearance, but in atomic structure, specific gravity, mobility, hardness, capillary development, and other properties. He will learn in what way each constituent contributes to pore and capillary development and to the formation of gel and crystals. He will obtain a clear picture of the mechanism by which strength is developed, with special regard for the part played by those constituents which are lost from the cement grain to crystallise in the pore spaces and perhaps leave capillaries in the grain in so doing, and the part played by the hydrated and gelatinous portion which remains attached to the core of the grain through the years. The effect of crystal size, grain size, impurities, temperature variations, and a multitude of other factors will be systematically studied.

Research will not be limited to peering within the cement grain. Further improvement will be made in increasing cement efficiency but with more emphasis placed on attempting to permit the minimum cement content which makes durable concrete of minimum change in volume, rather than high strength. The effect of controllable factors from the limestone and clay to the finished cement will be investigated. Some of the factors which seem most worthy of study at the present time are (1) modification of composition to reduce the percentage of non-cementing constituents, (2) heat treatment of hot clinker to improve grindability and to modify the structure of the ultimate cement grain, (3) control of atmosphere in kiln and cooler, (4) treatment of cooled clinker to modify its properties and especially to alter the tricalcium aluminate, (5) addition of small amounts of reagents in the finish grind to improve grinding and to improve hydration properties of the cement, (6) control of particle size through the use of air separators to eliminate both the coarsest and finest particles, and (7) removal of impurities which affect the surface condition and general hydration characteristics of cement grains.

While a cement of greater efficiency is worth more to the consumer, it is not likely that he will pay more for it. The manufacturer will probably get his reward through an unprecedented volume of business and through the economy of manufacture which results from his researches, either directly or indirectly. Thus, both the cement user and the manufacturer will profit by the researches which have already begun, and the general public will be benefited by having safer and more beautiful crack-free buildings.

Granulometric Composition of Cement.

A REPORT of the U.S. Bureau of Standards states that although a great deal of work has been done to determine the effect of fineness of grinding of cement on the properties of neat pastes, mortars, and concretes made therefrom, there has not been enough data available to allow many broad generalisations other than that fineness of grinding is an important factor in determining the rate of increase in strength, and that there is urgent need for further study. An investigation has been undertaken at the Bureau with the hope of clearing up some of the controversial issues. In this study six different cements were separated into size fractions, and studies were made of the individual fractions as well as four different blends of them.

It was found that the finest material in a cement, such as that of diameter less than 7 microns, is very valuable because of the plastic qualities which it confers upon the concrete mixes and also because of the large contribution which it makes to early strength. Materials of sizes larger than 7 microns were found to be increasingly deficient in plasticity; a 7 to 22-micron fraction was not very different from an ordinary cement, while a fraction of material greater than 55 microns in diameter behaved very much like a fine sand. The strengths of mortar briquettes and concrete cylinders made from four fractions of material coarser than 7 microns were found to decrease with increasing grain size, or to increase with increasing specific surface, at all ages tested.

Four cements blended from the fractions in varying proportions so as to have specific surfaces ranging from 1,350 to 3,300 square centimetres per gramme developed strengths directly related to the specific surface at all ages. The neat pastes of these cements, on the average, required an amount of water for normal consistency almost directly related to the specific surface. The time of initial set as determined by the Gillmore needle was found to be inversely related to the specific surface.

A more thorough analysis of the strength data tended to prove that the compressive strength of concrete is very nearly a direct function of the amount of cement which has become hydrous. No direct measurements of the rates of reaction were made, but a function of size distribution was found which could logically be expected to represent the amount of cement which had become hydrous and which yields values proportional to the strengths of the fractions and also those of the blends. When the compressive strengths were plotted against specific surface one line was obtained for the blends and another for the fractions, but when they were plotted against the supposed hydrous material only one line was obtained.

The contribution of the 0 to 7-micron fraction to the compressive strengths of the blended cements was calculated by an algebraic method based on the assumption that the contribution of any fraction to the strength of a blended

cement is equal to the product of the decimal part of the blend composed of that fraction and the strength of the fraction when tested by itself. The calculated values were of the order which might have been expected, and it is believed that they indicate the actual worth of the fine material much more closely than values determined by testing the fraction alone with the low cement-water-ratio which was required by the fine material.

Reaction Between Blast-furnace Slag and Water.

EXPERIMENTS carried out by F. Kaempfe according to the methods developed by T. Wang for cement, in which grit of between 88 and 120 microns diameter instead of fine material was shaken with water or aqueous solutions, and the new compounds determined in the decanted liquid, are described in a recent issue of *Zement*. The following results were obtained :

Pure water produced no swelling or separation of new compounds, but activating solutions produced a strong reaction. The alkaline activators depend on the combination of calcium hydroxide and the sulphate activators on calcium sulphate. Activators act chiefly on the aluminates in the slag. Alkaline activators form basic hydrated calcium aluminates, and the sulphate activators calcium sulphoaluminate. This is in agreement with practice where it is found that the slags which are low in alumina have low hydraulic properties. The silicates hydrate to hydrated calcium silicates with a lime-silica ratio of 1 to 1.5. With alkaline activators the concentration of calcium hydroxide in the liquid phase is very much lower than that obtained when Portland cement is used. Besides calcium sulphide, small amounts of free sulphur were found in the slag. Calcium sulphide assists hydration since calcium hydroxide, which is given off during its hydrolysis, acts as an activator. The free sulphur reacts with calcium sulphide in solution to form calcium polysulphide and with calcium hydroxide to form calcium thiosulphate. The polysulphide changes to thiosulphate in the presence of calcium hydroxide. These reactions remove lime from solution and therefore retard hydration.

Since the formation of polysulphide retards or completely stops hydration, care must be taken to have enough lime present so that the ratio of sulphur to calcium in the liquid phase does not exceed 2 : 1. The presence of sulphur in the new compounds makes it likely that a complex hydrated calcium-aluminate-sulphide is present. When the slag is mixed with the solution there is at first a strong reaction with the formation of a gel coating on the grains, causing the reaction to slow down ; when the coating has attained a certain thickness it is broken off during the shaking and the reaction proceeds again. If sufficient lime is present the same compounds are formed with alkaline activators as appear in the hydration of Portland cement.

Effects of Fluorides Upon the Thermal Synthesis of Calcium Silicates.

By S. NAGAI and Y. KOSAKI.

PARTS VI and VII of the report describing this series of researches are now available. In the previous reports the results of studies on the effects of calcium fluoride (CaF_2) on thermal syntheses of calcium silicates $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot 2\text{SiO}_2$ and $\text{CaO} \cdot \text{SiO}_2$ were reported. In these studies the degree of combination between lime and silica was measured only by the ratios of combined lime to combined silica or their molecular ratios, and it was ascertained whether calcium silicate was principally produced by comparing the values of these ratios with the theoretical values of lime to silica of (1) $3\text{CaO} \cdot \text{SiO}_2$:2.80 or molecular ratio 3.00, (2) $2\text{CaO} \cdot \text{SiO}_2$:1.87 or molecular ratio 2.00, (3) $3\text{CaO} \cdot 2\text{SiO}_2$:1.40 or molecular ratio 1.50, and (4) $\text{CaO} \cdot \text{SiO}_2$:0.93, or molecular ratio 1.00. In practice, it was often observed that these four calcium silicates were simultaneously produced and contained in the same sample in several proportions. The method described is therefore not applicable, and should be corrected. M. Jander and E. Hoffmann ("Zeit. fuer angew. Chem.," 1933, 46, 76) described a method of measuring these four calcium silicates, namely, the modified fractional dissolution method formerly proposed by Mr. Nagai in studies on the hydrothermal syntheses of calcium hydrosilicates ("Zeit. fuer anorg. und. allgem. Chem.," 1932, 206, 177 and 207, 321). This method was applied to the present studies and clear results were obtained.

Pure calcium carbonate and silicic acid anhydride were intimately mixed in the molecular proportion of 2 to 1. This mixture $2\text{CaCO}_3 : \text{SiO}_2$ (2 : 1) or $2\text{CaO} : \text{SiO}_2$ (2 : 1) was heated at 1,000 to 1,400 deg. C. for one hour, and the heated products were treated in the following manner: (1) Determination of free lime by titration with ammonium acetate-alcoholic solution in the mixed solution of glycerol and alcohol, (2) Determination of the sum of free lime and combined lime of $3\text{CaO} \cdot \text{SiO}_2$ and $2\text{CaO} \cdot \text{SiO}_2$ by titration with 0.1N hydrochloric-acid-methyl alcoholic solution in the mixed solution of *o*-nitrophenol- and methyl alcohol, (3) Determination of the sum of free lime and combined lime of $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, and some part of $3\text{CaO} \cdot 2\text{SiO}_2$ by titration with 0.1N hydrochloric acid solution in water, (4) Determination of silica of $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, and some part of $3\text{CaO} \cdot 2\text{SiO}_2$ from the filtrate after the titration described in (3), (5) Determination of the sum of lime from $\text{CaO} \cdot \text{SiO}_2$ and residual part of $3\text{CaO} \cdot 2\text{SiO}_2$ and also the sum of silica of these calcium silicates by treating the filtration residue in (4) with 2 per cent. hydrochloric acid solution, and (6) Determination of uncombined or free silica from the residue of the acid treatment described in (5).

From these data the amounts of (a) free lime, (b) uncombined or free silica, (c) individual amounts of four calcium silicates, $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot 2\text{SiO}_2$

and $\text{CaO} \cdot \text{SiO}_2$, (d) the sum of these four silicates, and (e) the molecular ratio of combined lime to combined silica were calculated. From the results, the mechanism of formation of four calcium silicates by several heating conditions are clearly observed. As mentioned, the values of molecular ratio of combined lime to combined silica are equal in the last four samples, but the proportion of four calcium silicates produced is different; dicalcium silicate, $2\text{CaO} \cdot \text{SiO}_2$, increases and is most favourably produced by heating at 1,300 to 1,400 deg. C.

Next, 1 per cent. of calcium fluoride was added to the mixture $2\text{CaCO}_3 : \text{SiO}_2$ (2 : 1) and then heated in the same way. The remaining calcium fluoride in the heated product was determined. From these results several points are clearly observed as the effects of the addition of 1 per cent. calcium fluoride, i.e. (1) Tricalcium silicate $3\text{CaO} \cdot \text{SiO}_2$ is easily produced even at a lower temperature of 1,000 to 1,100 deg. C. by the presence of 1 per cent. CaF_2 , but its amount decreases gradually at higher temperatures of 1,300 to 1,400 deg. C. and changes to dicalcium silicate $2\text{CaO} \cdot \text{SiO}_2$. (2) The total amount of calcium silicates produced is considerably greater than those produced without 1 per cent. CaF_2 . (3) Dicalcium silicate is also produced in far greater amount with 1 per cent. CaF_2 . (4) The same degree of combination is attained by the addition of 1 per cent. CaF_2 even at about 150 deg. C. lower temperature. (5) The amount of CaF_2 remaining in the heated products is 75 to 80 per cent. of the added amount (1 per cent. of the mixture $2\text{CaCO}_3 : \text{SiO}_2$ corresponds to 1.51 per cent. of the calcined mixture $2\text{CaO} : \text{SiO}_2$), which is nearly equal to those already obtained in a previous investigation.

Further investigations were undertaken on the effects of (a) Longer heating with or without calcium fluoride, (b) Larger amount of calcium fluoride, (c) Mixture of higher lime content $3\text{CaO} : \text{SiO}_2$ (3 : 1) with or without calcium fluoride, etc.

The mixture $2\text{CaO} : \text{SiO}_2$ (2 : 1) was heated at 1,200 deg. C. with or without 1 per cent. calcium fluoride, changing the heating time from 0.5 hour to 4 hours. The heated products were studied by the same method adopted in the preceding report.

By comparing the results the following facts are seen, (a) prolonged heating time, even to 2 to 4 hours, is not so effective, owing to the low temperature and the absence of calcium fluoride; (b) the addition of 1 per cent. calcium fluoride is highly effective for the formation of calcium silicates, especially the silicates of higher lime content ($2\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{SiO}_2$); (c) total amounts of calcium silicates produced are about 20 per cent. more if 1 per cent. calcium fluoride is present, so that the effect of the addition of 1 per cent. calcium fluoride allows the heating temperature to be reduced by about 150 deg. C.

Next, the authors studied the effect of the amount of calcium fluoride by changing its amount from 0.5 per cent. to 1 per cent., 2 per cent. and 5 per cent., and heating at 1,200 deg. C. for one hour. The effect of calcium fluoride was clearly observed in the sample which contained 0.5 per cent. of calcium fluoride.

In the cases of samples containing larger amounts of calcium fluoride, the eutectic between $\text{CaO}-2\text{CaO} \cdot \text{SiO}_2-\text{CaF}_2$ prevents the complete combination, which is more clearly seen in the following studies of heating the mixture of higher lime content ($3\text{CaO} : \text{SiO}_2$ (3 : 1)), with 2 to 5 per cent. calcium fluoride.

The second mixture of high-lime content $3\text{CaCO}_3 : \text{SiO}_2$ (3 : 1) or $3\text{CaO} : \text{SiO}_2$ (3 : 1) was also treated with and without 0.5 to 5 per cent. calcium fluoride, by changing the heating conditions and the products were analysed by the fractional dissolution method of Jander and Hoffmann.

(A) Heating temperatures changed from 1,000 deg. C. to 1,400 deg. C.; heating time fixed at one hour and without calcium fluoride. (B) Heating temperatures changed from 1,000 deg. C. to 1,400 deg. C.; heating time fixed at one hour and with 1 per cent. of calcium fluoride. By comparing these results the most remarkable point is the result of the sample in which the percentage of tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$), increased to 83 per cent. and dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$) decreased to 5 per cent.; the most effective temperature for the formation of tricalcium silicate by the addition of calcium fluoride is perhaps 1,250 to 1,300 deg. C., which is the most important point in the burning of Portland cement clinker with the addition of fluorspar.

(C) Heating temperature fixed at 1,200 deg. C.; heating times changed from 0.5 hour to 4 hours and without calcium fluoride. (D) Heating temperature fixed at 1,200 deg. C.; heating times changed from 0.5 hour to 4 hours and with 1 per cent. calcium fluoride. In these two series of experiments, the effect of prolonged heating was studied with and without the addition of 1 per cent. calcium fluoride at a temperature a little lower than the most effective obtained in (A) and (B). The heating temperature of 1,200 deg. C. is not high enough to complete the combination, even by the prolonged heating of 2 to 4 hours and by the addition of 1 per cent. calcium fluoride; the heating temperature must be higher than 1,250 to 1,300 deg. C. for the complete formation of tricalcium silicate even in the presence of calcium fluoride.

The Hardening of Cement. By L. Jesser. *Zement*, pp. 665, 677, 691, 1934.—When two elements made of the same metal are immersed in Portland cement or sorel cement mortar a difference of potential is established between them, which rises to a maximum a few hours after gauging the mortar and then falls later. The metal must be capable of reacting with the liquid phase in the mortar. This phenomenon indicates that the setting and hardening of cement is of an electrochemical character. A number of experiments has been carried out to elucidate this phenomenon, and it has been found to be caused by the difference of potential due to the existence of a colloid, the actual difference of potential occurring between the solid and the liquid phases. A theory of hardening is developed and applied to sorel, Portland, aluminous, and slag cements.

Efflorescence in Concrete.

THE scum, or efflorescence, which sometimes forms on brick or concrete buildings, is usually caused by excessive dampness. Chemical examination usually provides a definite clue as to its cause. Very few cases of chemical examination of efflorescence on concrete are recorded, but in the majority of cases the scum consisted of calcium carbonate. This probably arises from the Ca(OH)_2 liberated during the setting of the cement being brought to the surface under damp conditions as a result of capillary action and porosity. In time it is converted into an insoluble white scum of CaCO_3 due to the action of the CO_2 in the atmosphere. Concrete products may, in some cases, have continuous pores through which Ca(OH)_2 in suspension may also pass. The porosity of the mortar plays a large part in regulating efflorescence. In a very porous material the soluble salts may crystallise partly in the interior of the mortar whereas with material of closer structure the salt-saturated water is forced to the surface. There would thus appear to be an optimum point of porosity to ensure the minimum of efflorescence. It has been suggested that the efflorescence shown by coloured cement ware is due to alkali salts from the ash of the coal used in burning the clinker and is merely made evident by the colour and not caused by it.

Apart from the abstraction of lime from the cement, efflorescence is very often traced to soluble matter contained in the aggregate. This has been more particularly noticed in work where sea sand and broken brick have been used as aggregate. The composition of the efflorescence depends on the nature of the water-soluble salts contained in the aggregate, and the presence of excessive quantities of compounds other than calcium carbonate indicates that the aggregate requires washing before being mixed with the cement.

The conditions favouring the formation of efflorescence are : (1) The concrete is too porous ; (2) too much gauging water has been used ; (3) a head of water at the back of the concrete ; (4) dirty aggregate. If the aggregate contains no soluble matter, and if a dense concrete is made up with the proper quantity of water, the risk of efflorescence on concrete should be minimised.

Various substances for mixing with the concrete have been suggested with a view to reducing the possibility of efflorescence. Barium carbonate and barium hydrate prevent efflorescence due to calcium and magnesium sulphates, but do not prevent scum arising from hydrated lime. The addition of 5 per cent. BaCO_3 to the cement before mixing has been found to give good results where conditions are very favourable to efflorescence, and the strength of concrete is not affected by additions up to 5 per cent. Although Ba(OH)_2 is as effective as BaCO_3 it is too expensive for commercial use. BaCl_2 is ineffective in preventing efflorescence since it is soluble in water, and any excess is liable to travel to the surface and so increase efflorescence. A suspension of BaCO_3 in barium bicarbonate solution has been recommended as being more effective than BaCO_3 alone. Barium fluoride free from hydrofluoric acid has also been suggested

since it is less expensive than $\text{Ba}(\text{OH})_2$ and is more soluble than BaCO_3 and will thus come into closer contact with the injurious compounds.

Additions of diatomaceous earth or trass to the cement are said completely to prevent efflorescence¹. These substances probably combine with the hydrated lime to produce an insoluble silicate. Ammonium carbonate added either to the cement or gauging water is also stated to prevent efflorescence, and is moreover said to exert a favourable influence upon the setting of the cement.

A solution of the problem of efflorescence may be found in the development of an ideal waterproofing compound which will fill the voids of the concrete and thus prevent the salt-laden water being drawn to the surface by capillary action. In recent years it has been suggested that efflorescence in concrete is more pronounced because modern cements contain much more free lime than the cements of thirty years ago. In addition, finer grinding causes greater shrinkage during setting and hardening. Examination of modern cements shows, however, that there is no reason to believe that they contain more free lime than the early cements.

A certain amount of evidence has been obtained to show that efflorescence in concrete is largely due to its alkali content derived from the cement. The alkali content of modern cements may range from 0.6 to 1.4 per cent., the leaching out of which would form a considerable scum on the surface of the concrete.

Lubrication of Haulage Ropes.

It is by no means unusual for a haulage rope to be left without lubricant because, it is argued, of the impossibility of getting oil to adhere. The result of neglecting to apply an external lubricant is that external wear is more rapid, and once the internal lubricant, if any, has been squeezed out, the rope is liable to internal as well as external corrosion. When wear takes place in the presence of corrosion, its severity is greatly enhanced because the products of corrosion act as abrasives and the wear continually exposes fresh surfaces to corrosion. Even in the absence of corrosion, severe wear may lead to deterioration by hardening of the surfaces of the wires. It has been proved by laboratory experiments that the presence of a film of oil is effective in preventing hardening.

Before the lubricant is applied, the surface of the rope should be cleaned and dried, because oil or grease applied to the surface of a rope covered with mud or coal dust, water and old oil will be thrown off without having the slightest chance of penetrating to the interior. In most cases the treatment can be given to the rope during an idle shift.

Main ropes used on inclines can be treated as follows. The rope should be wound very slowly on to the drum, the surface being cleaned as it enters the engine house. Cleaning should be done with wire brushes without using a solvent, such as petrol or paraffin. The brushes may from time to time be washed in paraffin, but this should be shaken off before using the brush on the

¹Tonind. Ztg., 37, 1856.

rope again. The cleaning may be completed with waste or sacking. No solvent (petrol or paraffin) should be used on the rope, because experience has shown that the solvent readily penetrates into the middle of the rope and rapidly dissolves out any remaining lubricant. The rope should be allowed to remain on the drum long enough to allow it to dry as much as possible.

When the rope has been cleaned and dried, the lubricant should be applied by hand with a fairly stiff brush. Devices in which the rope is caused to pass under a roller in a bath of oil are less effective and are wasteful. It is important that the rope should be dry when the lubricant is applied otherwise the oil will not adhere, and the work should be done within the engine house as the rope leaves the drum. If the lubricant is applied in the open, a shower of rain may render useless the whole operation of cleaning and drying the rope. The successful lubrication of a haulage rope calls for a good deal of skill and patience, but unless it is properly done the time and materials are wasted. It is better to do a portion of the rope well each week than to waste a lot of grease by applying it to the whole of the rope without cleaning and drying.

It is not possible to lay down any fixed periods for the lubrication of haulage ropes, because the periods will vary with the working conditions. A rope which makes a large number of journeys on a wet incline will need lubrication every week, whereas a rope which makes only a few journeys in the dry may be kept in good condition by less frequent treatment. Excellent results have been obtained on endless rope haulages where the rope is lubricated continuously. In one instance a light mineral oil is allowed to drip on to the moving rope at the rate of one drop per yard; this rope works on a comparatively clean and dry roadway.

Research is in progress as to the best type of oil for applying to ropes in service. At the moment it would seem that the best results are obtained with a medium heavy mineral oil. The oil must be free from acidity, and should contain no filler or soapy material. (From S.M.R.B. pamphlet No. 92, "The Deterioration of Haulage Ropes in Service.")

Raw Material Fineness and Lime Saturation of Clinker. By G. Mussgnug. *Zement*, p. 1, 1935.—The effect of the fineness of the raw material on the lime saturation of clinker for various raw materials has been studied. The basis of the investigation was the determination of the free lime in the product. It is shown that the fineness of the raw material, particularly for raw materials of widely differing composition, has a considerable effect on the lime saturation of the clinker. The chemical composition of the raw material and chiefly the amount of fluxes and brownmillerite present in the clinker play a very large part in the question of lime saturation. Blast-furnace slag in the presence of a certain amount of flux has a greater reactivity than natural argillaceous raw materials with about the same amount of flux. Hence in practice a higher lime saturation is reached with blast-furnace slag as a raw material than with natural raw materials.

Recent Patents Relating to Cement.

425,048.—Portland Cements. Pontopidan, C., 90, Vejlesovej, Holte, Denmark. Sept. 5, 1933.

In the manufacture of Portland cement the calcareous material is less finely ground than is usual for normal Portland cement, the clay is either coarsely or finely ground, and the materials are burned in the kiln in such a manner that some of the lime remains uncombined, this free lime in the clinker being then changed to calcium hydrate without substantially hydrating the cement, e.g., by treatment with steam at 170 to 400 deg. F. during or after the grinding. The coarsely crushed and pulverised calcareous material can be mixed with the clay before it enters the kiln, and the mixture may be dry, semi-dry, or in a slurry state. The mixture is not finely ground together, but if desired the calcareous material may be coarsely pulverised together with the clay. In no case will the residue of raw mix on a No. 170 sieve be less than 20 per cent., and in general it will be between 20 and 45 per cent. Instead of mixing the materials before entering the kiln, the clay may be fed in separately, e.g., by being blown into the kiln by preheated air. The resulting cement may be divided by passing it through a separator into two parts, one part containing a larger portion of the calcium hydrate than the original product and the other part containing a smaller portion.

424,614.—Pozzolan Cement. Wagner, H., 7, Im Kienle, Stuttgart, Germany. —(Assignee of Siemering, R.; 21, Nussbaumallee, Charlottenburg, Berlin). Oct. 5, 1934.

Miscellaneous Advertisement.

INVESTMENT.

Required. Practical man to invest £1,000 as third-share in small lime and cement business, or to purchase outright for £3,000. Plant includes small rotary kiln and modern crushing plant. Apply Box 1124, "Cement and Cement Manufacture," 20, Dartmouth Street, Westminster, S.W.1.

Pozzolan cement comprising a mixture of Portland cement or other highly calcareous hydraulic cement and burnt clay is made by burning the raw clay by means of the heat contained in the clinker of the calcareous cement and then grinding the clinker and burnt clay together. The raw clay, which may be first dried and ground, is fed, for example, at the burner end of a rotary kiln on to the incandescent clinker discharged from the kiln. The mixed mass falls into a rotary drum protected against heat loss where it is retained by a baffle for a sufficient time.

426,423.—Cements: Concentrating Ores.—Fuller Co., Calasauqua, Pennsylvania, U.S.A.—(Assignees of Breerwood, C. H.; Narberth, Pennsylvania, U.S.A.) Nov. 24, 1933.

In preparing a mixture of cement-forming raw materials from original materials all or a lime-bearing component of which contains lime and siliceous constituents, one of which is present in undesirable quantity, part of the original material is treated by froth flotation to separate the lime from the siliceous constituent, the excess is discarded, and the remaining treated material combined with the untreated part. Where the original materials contain silica in excess or in a form unsuitable for burning, at least part of the materials is subjected to classification to separate fine and coarse particles, and the latter treated by froth flotation to separate lime and silica, the latter being discarded. A micaceous limestone deficient in lime, after preliminary grinding is passed to finishing mills adjusted to give a coarser product than the normal. Owing to the greater hardness of the quartz present, the fines produced have an increased proportion of calcium carbonate. The discharge from the mills is separated by air or hydraulic classification and part of the tailings, the amount depending on the quantity of silica it is desired to discard, is treated by froth flotation.

It is preferred to form a pulp with an excess of water so that deleterious materials are removed with the overflow, the flotation agent being equal parts of

oleic acid and cresol present in an amount of about $1\frac{1}{2}$ lb. per ton of tailings. The calcite is floated off and the deposit in the cells may be separated by a concentration table to obtain the iron if its addition to the final cement mixture is necessary. In some cases, a second flotation operation is effected and, by concentrating the residue, pure silica is obtained as a by-product. The calcite is dried, if necessary, and returned to the finishing mills with the other constituents.

In a modification, the separation is effected before the materials are fed to

the finishing mills. Where the original materials comprise at least two components, for example, a marl or chalk and a clay or shale, it may be necessary to treat one component only if the other does not contain coarse silicas. This component is classified, the coarse particles treated by flotation, and the silica discarded. Alternatively both components may contain coarse silicas, in which case relative quantities thereof are treated so that the excess silica is equal to the total amount of coarse silicas.

Special Cements. By W. G. Czernin. *Tonind. Zeit.*, p. 1245, 1934.—Since tricalcium aluminate in cement causes weakness in sulphate waters, cements with very low alumina content such as ore cement were developed. Lately it has been found that the same object is attained by adjusting the composition so that there is at least one molecule of Fe_2O_3 for every molecule of Al_2O_3 , so that $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$ is formed instead of $3\text{CaO}.\text{Al}_2\text{O}_3$. Tricalcium aluminate has a bad effect on the swelling and shrinkage of cement. It also confers on cement a larger heat of hydration. Tricalcium aluminate gives a high strength to cement at early dates but not later on. It is clear that if a cement with a high resistance to corrosion, low shrinkage, and low heat of hydration is required the tricalcium aluminate must be cut down to a minimum and substituted by $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$ by the addition of iron oxide to the raw materials.

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